



Electrochemical properties of electrospun polyindole nanofibers as a polymer electrode for lithium ion secondary battery

Cai Zhijiang^{a,b,*}, Shi Xingjuan^a, Fan Yanan^a

^a School of Textiles, Tianjin Polytechnic University, Tianjin 300387, China

^b Key Laboratory of Advanced Textile Composites, Ministry of Education of China, Tianjin 300387, China

H I G H L I G H T S

- Polyindole nanofiber is fabricated by electrospinning using acetonitrile as solvent.
- A lithium/polyindole nanofiber battery is constituted by using polyindole nanofiber.
- The lithium/polyindole nanofiber battery achieves 83–75 mAh g⁻¹ discharge capacity.
- The battery has excellent cycle property and fast charge/discharge performance.

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Polyindole nanofiber is prepared using electrospinning technique for the first time and evaluated as cathode active material for application in lithium ion battery. Surface morphology of the cathode is studied using scanning electron microscope. It shows porous structure constructed by nanofibers with diameter ranged from 347 nm to 180 nm. Electrochemical evaluation of the Li/polyindole nanofiber battery shows good cycling properties as well as fast charge and discharge properties. The battery achieves about 3.0 V electromotive force with discharge capacity of 83 mAh g⁻¹ which is about 99% of theoretical value. There is slow capacity fading during cycling and the discharge capacity drops to 72% of theoretical capacity after 500 cycles at discharge current density of 40 mA g⁻¹. At higher discharge current density like 200 mA g⁻¹ and 400 mA g⁻¹, the cell still can deliver stable discharge capacity of 79 mAh g⁻¹ and 70 mAh g⁻¹. Temperature performances test of the Li/polyindole nanofiber battery shows that the discharge capacity of the Li/polyindole nanofiber battery increases with temperature increasing. In summary, the test results have proved that polyindole nanofiber is a good candidate as cathode material for lithium ion battery.

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1. Introduction

Electrically conductive polymers have attracted much interest in the past 20 years because they simultaneously display the physical and chemical properties of organic polymers and the electrical characteristics of metals. The main work of conductive polymers focuses on heterocyclic conducting polymers containing nitrogen atoms like polyaniline, polypyrrole, polycarbazole and their substituted derivatives. They have also been investigated for many industrial applications such as electrochromic displays [1],

electromagnetic shielding [2], actuators [3], chemical sensors [4] and polymer batteries [5] due to their interesting electrical properties and long-term ambient stability.

Polyindole is a conducting electroactive polymer, which can be obtained by electrochemically oxidation of indole in various electrolytes and chemical polymerization by oxidants. Polyindole possesses the properties of both poly(para-phenylene) and polypyrrole together, such as fairly good thermal stability [6], high-redox activity and stability [7], slow degradation rate in comparison with polyaniline and polypyrrole [8], and an air stable electrical conductivity close to 0.1 S cm⁻¹ in the doped state [9]. Moreover, polyindole compounds are known to exhibit higher redox potential compared to polyaniline and polypyrrole [10]. Pandey has reported a secondary battery using polyindole as active material in aqueous neutral electrolyte [11].

* Corresponding author. No 399 BingShuiXi Street, XiQing District, Tianjin 300387, China. Tel.: +86 22 83955385; fax: +86 22 83955187.

E-mail address: caizhijiang@hotmail.com (C. Zhijiang).

Electrospinning technique provides a versatile and effective method to prepare fibers with the diameters ranging from the nano- to micro-meter scale. The electrospun fibers have exceptionally long length, uniform diameter, high porosity, interconnectivity, interstitial and large surface to volume ratio, which can be applied in membrane filtration technology [12], tissue engineering [13] wound dressings [14], optical sensors and biosensors [15], and nano-particle carriers in controlled drug release [16].

Nowadays, fabrication of nanofibers made of conductive polymers has been reported in the design and construction of electrochemical devices [17]. The nanofibers with high specific surface area are advantageous as electrode for the energy storage devices such as batteries and capacitors [18–20]. The high specific surface area of electrode brings high utilization of the electrochemical active materials and high charge–discharge rate to batteries and capacitors.

In our previous work, we introduced a polyindole-based Li-polymer secondary battery system [21] using polyindole powder as active electrode materials. In the present study, we apply the electrospinning technique for the construction of polyindole nanofiber electrode. We prepare the Li/polyindole nanofiber battery using electrospun polyindole nanofiber as cathode active material. The morphological characteristics of the polyindole nanofiber electrode are observed by scanning electron microscopy. The electrochemical performance of the polyindole nanofiber electrode is investigated with cyclic voltammetry technique and the electrical resistance test. The performance of Li/polyindole nanofiber battery is evaluated in terms of charge–discharge test at different current density, durability test and temperature performance.

2. Experimental

2.1. Materials

The materials used in this investigation and their sources are as follows: indole was obtained from Aldrich Chemical Co., LTD.; chloroform and ammonium peroxydisulfate were obtained from Sigma Chemical Co., LTD. and used as received. All other chemicals employed were of analytical reagent grade. Li electrode was kindly provided by Tianjin LiSheng Power Sources Co., LTD.

2.2. Polymerization of indole

The synthesis of polyindole was carried out by the following procedures. The reactor used was a 4-necked 500 ml round-bottom flask, provided with a stirrer and was placed in a thermostatic bath. It was purged by a cycle comprising of placing under vacuum 3 times and rinsing 3 times with pure and dry nitrogen. 180 ml of chloroform, previously degassed with nitrogen, was introduced into this round-bottom flask, which was kept at 25 °C under nitrogen, and 35 g of ammonium peroxydisulfate was then filled with 5 ml of demineralized water and the reservoir with a tap was filled with 20 ml of chloroform and 3.6 g of degassed indole. The water, using a syringe, and the chloroform and indole, using the reservoir with a tap, were then introduced in parallel into the flask in the course of 10 min. The molar ratio of ferric chloride to indole was 5. The flask was then kept at 15 °C for 5 h, with stirring; the pH of the reaction mixture is 1.50 ml of water was then introduced into the flask, which was kept at 15 °C, in the course of 45 min. The product, which at this stage was in the form of a suspension, was filtered under air at 20 °C. The product obtained was washed 4 times with 100 ml of water at 20 °C and then dried overnight under vacuum at 20 °C under 2670 Pa.

2.3. Electrospinning of polyindole

Polyindole solution was prepared by dissolving polyindole powder in acetonitrile under ultrasonication and then filtered through Teflon membrane filter. Electrospinning of polyindole was then carried out as the following procedures. Polyindole solution was filled into a glass syringe terminated by a stainless steel needle whose inner diameter is 0.35 mm. The syringe was placed in an automatic pump and polyindole solution was extruded out at a constant speed of 0.8 ml h⁻¹. High voltage ranging from 16 to 24 kV was applied in the electrospinning process. The tip-to-collector distance was fixed at 20 cm. The polyindole nanofibers were collected by conductive carbon paper. The experiment was done in an environmental chamber with constant temperature at 25 °C and the relative humidity (RH) at 35%. Electrospinning parameters and sample code are listed in Table 1.

2.4. Preparation of Li/polyindole battery

The simple experimental electrochemical cell was composed of polyindole nanofiber cathode, lithium metal anode, the glass filter separator, and 1 M LiPF₆ in EC:DMC (1:1 in volume) as electrolyte solution. They were sequentially accumulated like a sandwich by using a test holder in a dry box.

2.5. Characterization

Viscometer (Brookfield Corporation DV-II) was used to measure the viscosity of polyindole solution prior to electrospinning. The morphological and phase analysis for the obtained polyindole nanofiber were characterized by scanning electron microscopy (SEM, Model S-4200, Hitachi, Japan) and Fourier transformation infrared (FT-IR) spectroscopy (Perkin Elmer Spectrum RX-I). The Brunauer–Emmett–Teller (BET) surface area was measured by using a surface area analyzer (SAA: Sorptomatic 1990, Thermo-Finnigan Co.). The samples were degassed overnight in a vacuum at 100 °C, and N₂ gas was used. A relative pressure range, P/P_0 , of 0.05–0.3 was used for calculating the BET surface area.

2.6. Electrochemical properties

The polyindole nanofiber electrode resistance was determined by the AC impedance spectroscopy using a computer-aided Solartron 1260 Impedance/Gain-Phase Analyzer at frequencies of 10 mHz–1 MHz. All the measurements have been made at room temperature in air at zero DC current. The amplitude of the used sinusoidal signal was 10 mV. The results, obtained in the form of resistance, have been normalized for the geometric area and reported as area resistance. At least three measurements were taken for each sample and average values are reported in the paper. The electrochemical measurements were performed with a Solartron electrochemical interface (model 1287 Solartron UK) connected to a PC through the serial port. The cyclic voltammetry test was carried out in a three-electrode single-compartment cell using Pt gauge, a saturated calomel electrode (SCE) and polyindole

Table 1
Electrospinning parameters for polyindole.

Sample code	Concentration (%)	Viscosity (cP)	Humidity (%)	Temperature (°C)	Voltage (kV)
PI-1	2.0	800	35	25.3	16
PI-2	2.0	800	33	24.8	20
PI-3	2.0	800	34	25.1	24

(mass flow rate = 0.8 ml h⁻¹, the inner diameter of the needle = 0.35 mm, tip-to-collector distance = 20 cm).

nanofiber electrode as counter, reference and working electrode, respectively. The charge/discharge test of the Li/polyindole battery was performed using a galvanostatic charge/discharge cyler in the cut-off voltage range from 2.0 V to 4.0 V with different current density ranged from 40 mA g^{-1} to 400 mA g^{-1} . All experiments were carried out at room temperature ($20 \pm 2^\circ \text{C}$).

3. Results and discussion

3.1. SEM observation

In the electrospinning process, a suitable viscous solution is key point to make polyindole nanofibers. At viscosity lower than 500 cP, the solution is not viscous enough to electrospin a uniform fibrous structure. This is in the transition zone between electrospinning and electrospraying, which results in what is commonly referred to as a “bead-on-a-string” structure. At viscosity over 3000 cP, the solution is too viscous to flow through the nozzle. In the present work, polyindole solution with viscosity of 800 is used for electrospinning by controlling the concentration of polyindole solutions of 2.0%.

Fig. 1 shows the surface morphology of polyindole nanofiber electrode prepared by electrospinning under different conditions. The porous structure made by polyindole nanofiber can be observed and the polyindole nanofibers exhibit smooth surfaces, round shape and are randomly oriented. As we known, fiber diameter is dependent on many electrospinning variables including applied voltage and polymer concentration. By varying the applied voltage and polymer concentration, it is possible to modify the average fiber diameter of the electrospun nanofiber electrode. In the present work, the applied voltage is increased from 16 kV to 24 kV. The diameter of the electrospun fibers was measured by computer analysis using five SEM images for each sample. The average diameter as well as thickness and specific surface area are summarized in Table 2. With the applied voltage increasing, the average fiber diameter tends to decrease. The specific surface area is in the range of $57\text{--}75 \text{ m}^2 \text{ g}^{-1}$, depending on the fiber diameter. With the diameter of polyindole nanofiber decreasing, the specific surface area increases. The thinnest fiber with diameter of 186 nm can be fabricated in this work. By optimization the electrospinning parameters, thinner polyindole fibers with diameter less than 100 nm can be fabricated. This kind of work is ongoing in our lab and the results will be reported later.

3.2. FT-IR spectrum

Fig. 2 presents the FT-IR spectrum of polyindole nanofiber electrode obtained by electrospinning. The broad peak at 3409 cm^{-1} observed in the spectrum is the characteristic absorption of the N–H bond. The peak at 1580 cm^{-1} is ascribed to be the stretching and deformation vibrations of N–H bond and vibration modes of $\text{C}_2=\text{C}_3$ aromatic bonds. The peak at 1646 cm^{-1} is ascribed to the $-\text{C}=\text{C}-$ stretching vibrations on indole ring. Two sharp peaks at 741 cm^{-1} and 1459 cm^{-1} are assigned to the characteristic stretching modes of benzene ring in polyindole. The peak at 1366 cm^{-1} is related to modes involving the $\text{C}_8-\text{N}-\text{C}_2-\text{C}_3$ group. The peak observed at 1240 cm^{-1} signifies the heterocyclic ring stretching modes. The peak located at 1110 cm^{-1} is attributed to the vibration modes of C–N bond. The FT-IR spectrum can confirm the nanofiber electrode is made of polyindole.

3.3. Electronic conductivity

The area resistance is used to evaluate the electronic conductivity of polyindole nanofiber electrode made of PI-1, PI-2 and PI-3.

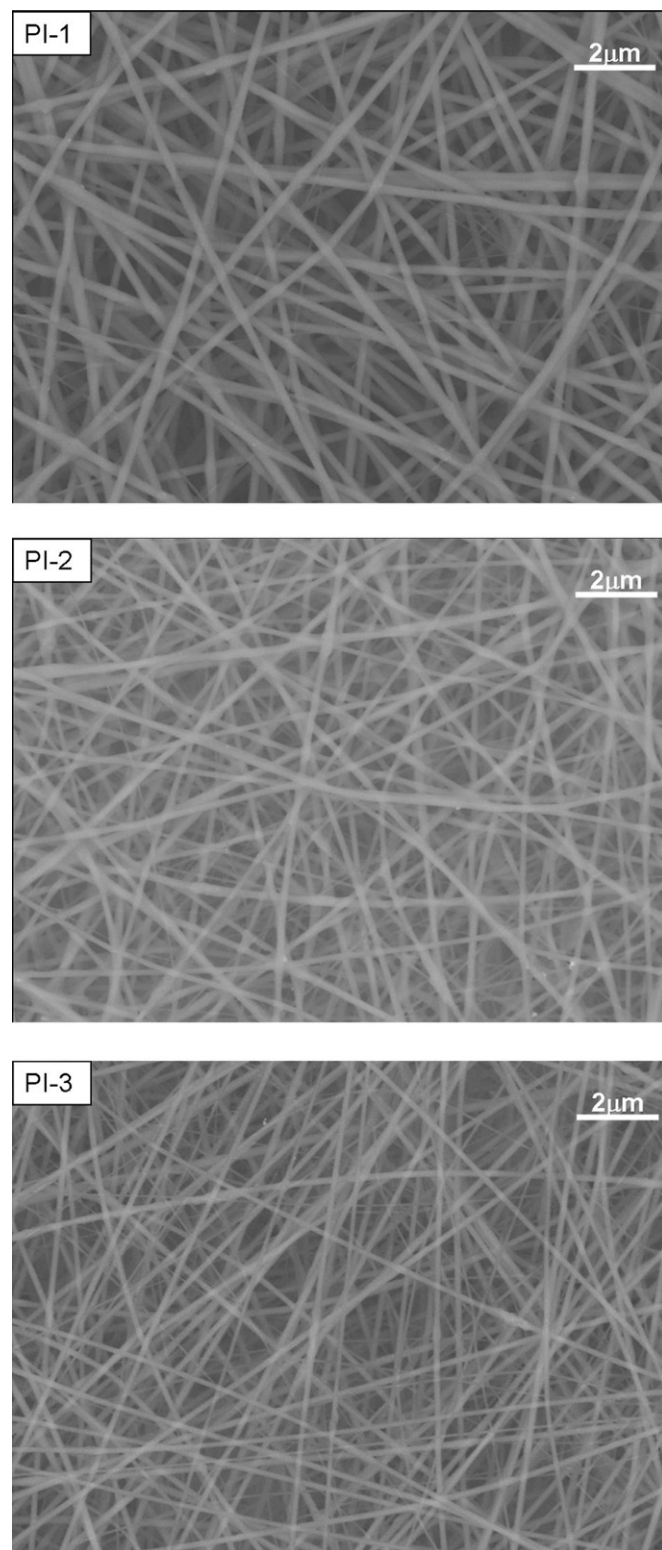


Fig. 1. Surface morphology of polyindole nanofiber electrode prepared by electrospinning under different conditions.

The results are shown in Table 2. As seen from Table 2, the area resistance of polyindole nanofiber electrode decreases with the average fiber diameter decreasing, which means the electronic conductivity has been improved. The area resistance of polyindole nanofiber electrode decreases from $8.44 \Omega \text{ cm}^2$ to $4.35 \Omega \text{ cm}^2$ when the average fiber diameter decreases from 347 nm to 186 nm.

Table 2
Physical properties of polyindole nanofiber electrode.

Sample code	Average fiber diameter (nm)	Specific surface area ($\text{m}^2 \text{g}^{-1}$)	Area resistance (Ωcm^2)
PI-1	347	57.43	8.44
PI-2	244	67.23	6.52
PI-3	186	75.33	4.35

This result indicates that the electronic conductivity of polyindole nanofiber electrode is affected not only by the intrinsic properties of the materials but also by the geometric structure of the fibers and electrode. In the present study, the electrode material and electrode shape are same. The only difference in polyindole nanofiber electrode is the diameter of the nanofibers. Thus, we can conclude that the diameter of polyindole nanofibers has important effect on electronic conductivity. The reason might be explained as following. The decrease of fiber diameter is believed to lead more compaction in the fiber, which results in better charge transport inside the fibers. At the same time, the decrease in fiber diameter allows the deposition of more fibers in a given volume. As a result, more fibers can provide more electronic paths usable for the conduction. As the polyindole nanofibers show significantly higher specific surface area together with higher electrical conductivity, it is expected to be more useful in various potential applications such as sensor or electrode materials for the rechargeable battery.

3.4. Cyclic voltammogram

Cyclic voltammetry (CV) provides both qualitative and quantitative information on electrode process. Fig. 3 shows CV curves of the polyindole nanofiber electrode made by PI-3, PI-2 and PI-1 between 0.2 and 1.2 V with a scan rate of 1 mV s^{-1} at room temperature in LiPF_6 containing electrolyte solutions. A multi-step redox process seems to be seen for polyindole nanofiber electrode with anodic peak at 1.0 V and cathodic peak at 0.8 V. It is known that the conductivity of a conducting polymer can be improved greatly by doping other ions. In this study, polyindole nanofibers, used for the cathode material of the battery, are in a state that PF_6^- ions are doped. The peak at 1.0 V corresponds to the oxidation (doping) and the peak at 0.8 V corresponds to the reduction (de-doping). For PI-1

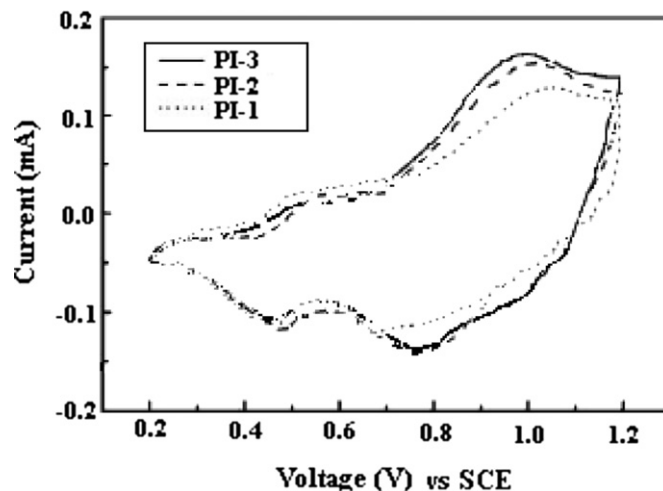


Fig. 3. Cyclic voltammograms of polyindole nanofiber electrode in LiPF_6 containing electrolyte solutions at room temperature (scan rate: 1 mV s^{-1}).

polyindole nanofiber electrode, the CV curve shows some difference in path and the redox peak shifted to 0.7 V. This phenomenon indicates that there are some difficulties in effective doping and de-doping process during cycling which may be due to less electrical conductivity and specific surface areas of polyindole nanofiber electrode used in the cell. Based on the CV test results, PI-3 shows the highest electrochemical activity. This result is in accordance with the electrical conductivity test results.

3.5. Charge/discharge test

According to the CV test results, the PI-3 is used as the polyindole nanofiber electrode in the experimental battery. The charge/discharge test of the Li/polyindole nanofiber cell is performed at a current of 40, 200, and 400 mA g^{-1} , which is about 0.5 C, 2.5 C and 5 C, respectively. The charging is terminated when a cut-off voltage (COV) of 4.0 V is reached and the discharge COV is set to 2.0 V. Fig. 4 shows the specific capacity curves during the charging and discharging periods of Li/polyindole nanofiber cell. During the charging process, the voltage increases slowly and the reduced polyindole is changed to its oxidized form. The cell voltage increases rapidly when polyindole oxidation is completed. A COV is existed to the charge voltage, and if it is exceeded, the corresponding overcharge leads to irreversible changes in the chemical composition and strong degradation in cell performance. These

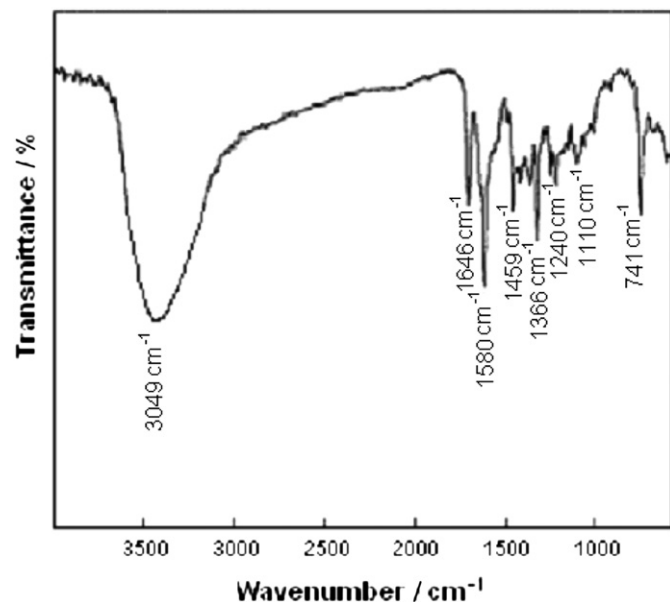


Fig. 2. FT-IR spectrum of polyindole nanofibers obtained by electrospinning.

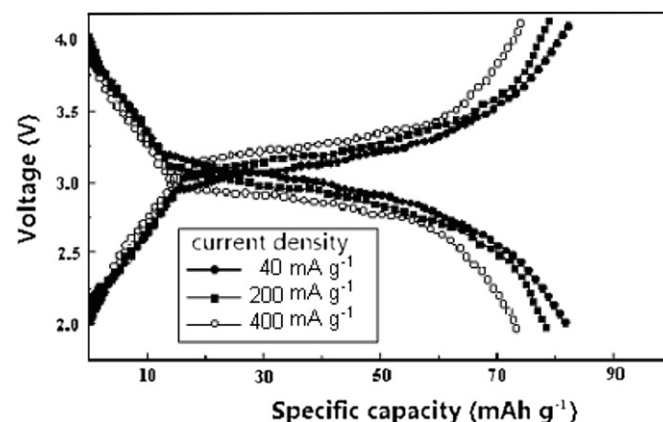


Fig. 4. The charge/discharge specific capacity curves of experimental Li/polyindole nanofiber cell at different current density at room temperature.

changes have been attributed to an over-oxidation process in the polymer. During the discharging process, the voltage falls first quickly and then shows plateau region around 3.0 V for a period of time. After that the voltage drops quickly again until the oxidized polyindole is changed completely to its reduced form.

The specific discharge capacity and energy density of the cell are calculated based on the discharge time, current density and the weight of polyindole in the electrode. The Li/polyindole nanofiber cell presents the discharge capacity of 83 mAh g^{-1} and energy density of 91 Wh Kg^{-1} at discharge current density of 40 mA g^{-1} . With the discharging current density increasing, the capacity and energy density of the cell decrease. For example, at discharging current density of 400 mA g^{-1} , the discharge capacity and energy density are 75 mAh g^{-1} and 83 Wh Kg^{-1} . The reason might be due to lower electrode polarization at smaller current density. In addition, with the discharging current density increasing, the plateau region of the cell decreases. For example, at discharging current density of 400 mA g^{-1} , the plateau region decreases from 3.0 V to 2.8 V. The discharge capacity maintains 90% of capacity relative to that at discharging current density of 40 mA g^{-1} . This result indicates that the Li/polyindole nanofiber battery is excellent in fast charge and discharge properties. Moreover, the capacity and energy density of Li/polyindole nanofiber battery are affected by the component of the electrolytic solution, diameter of nanofiber and charge/discharge current density. By optimization all these parameters, Li/polyindole nanofiber battery with better electrical performance can be achieved.

3.6. Temperature performances

The performance of the Li/polyindole nanofiber battery at various temperatures is an important issue for its potential applications. In this study, the charge/discharge test of the cell is carried out at the current density of 40 mA g^{-1} in the temperature region of -20°C to 60°C in the environmental chamber. Fig. 5 shows the specific discharge capacity of the cell at various temperatures. At 60°C and 40°C with current density of 40 mA g^{-1} , the capacity is near 120 and 100 mAh g^{-1} , respectively. Compared with the capacity at 20°C , the value increases about 45% and 25%. At 0°C and -20°C with current density of 40 mA g^{-1} , the capacity is about 61 and 26 mAh g^{-1} , which is about 72% and 31% of the capacity at 20°C . Variations in the capacity of polyindole nanofiber cell with

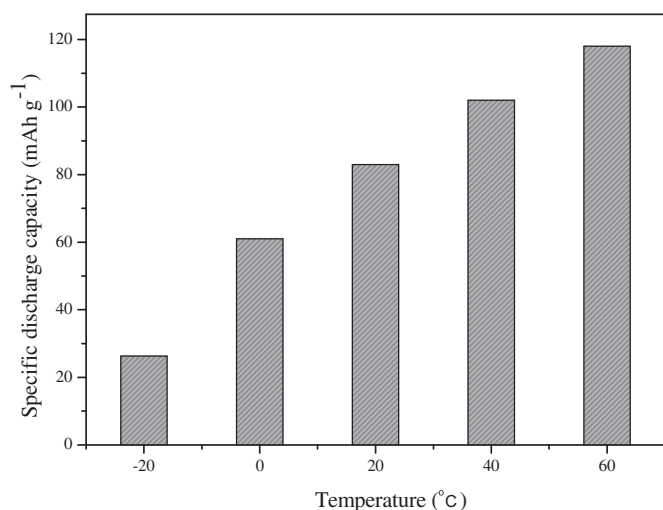


Fig. 5. The specific discharge capacity of the Li/polyindole nanofiber cell at various temperatures.

temperature have been attributed to the increase in the ionic conductivity of LiPF_6 and to the diffusion coefficient of the ions in the polymer. Since polyindole nanofiber cell performs better at elevated temperatures, it is possible that a battery based on this material could find numerous applications.

3.7. Durability test

Fig. 6 shows a cyclic property on repeated charge–discharge cycling at a charge and discharge current density of 40 mA g^{-1} . The cell achieves an initial discharge capacity of 77 mAh g^{-1} . With the cycling, the discharge capacity tends to increase and reach the highest value of 83 mAh g^{-1} at 30th cycle, which is about 99% of theoretical capacity of polyindole. During this process, the polyindole is fully activated and the capacity becomes stable. After cycling about 200 times, the discharge capacity exhibits a little decrease. This might be caused by a decay of the electrochemical activity of the Li/polyindole nanofiber battery. The discharge capacity reaches a minimum value of 61 mAh g^{-1} at 500th cycle, which is about 72% of theoretical value. The reason may be due to the irreversible loss of active material. This result indicates that the Li/polyindole nanofiber battery has good cyclic performance.

To further investigate the durability, surface morphology of polyindole nanofiber electrode is observed using scanning electron microscope after 500 cycles. Fig. 7 represents the SEM image of polyindole nanofiber electrode after cycling. The nanofibrous structure is still kept, while the diameter of nanofiber becomes a little bigger. There appears lots of etching pores on the surface of polyindole nanofibers. This may be due to the movement of ions get in and out the nanofibers during the charge/discharge period. The mass loss of polyindole will also lead to a decrease in capacity.

Cyclic property of the Li/polyindole nanofiber cell cycling at different current density is shown in Fig. 8. At current density of 200 mA g^{-1} , the cell delivers an initial discharge capacity of 73 mAh g^{-1} and keeps constant at a value of 79 mAh g^{-1} which is about 94% of theoretical value. At current density of 400 mA g^{-1} , the cell shows an initial discharge capacity of 70 mAh g^{-1} and reached a stable value of 75 mAh g^{-1} which is about 89% of theoretical value. These results show that the polyindole nanofiber can be used as active material for battery or supercapacitor where fast charge–discharge transfer takes place at the electrode material. The reason might be due to the unique structure of polyindole nanofiber

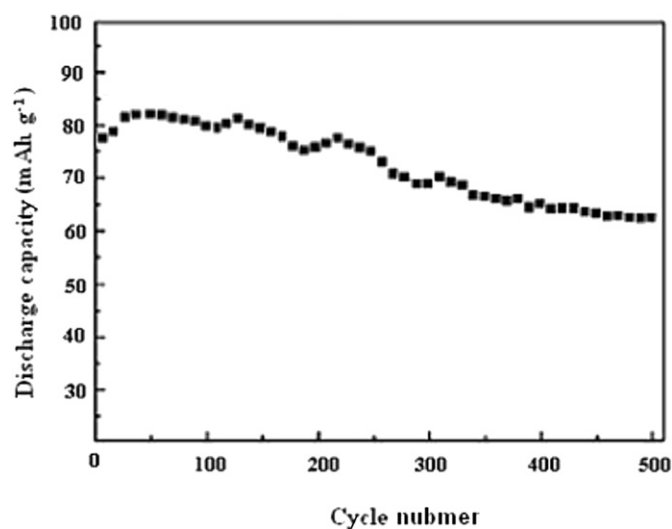


Fig. 6. The cyclic property of experimental Li/polyindole nanofiber cell at the current density of 40 mA g^{-1} .

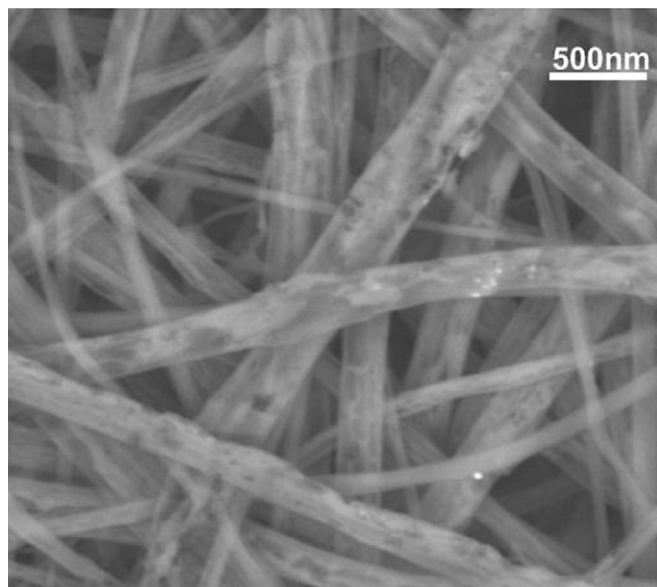


Fig. 7. Surface morphology of polyindole nanofiber electrode after cycling.

electrode. The porous structure provides a large surface area for the efficient intercalation reaction inside the cell and thereby maximum utilization of the active material which leads to maximum discharge capacity. The porous nanofibrous structure makes the ions free to move, allowing them to reach maximum active sites of the cathode. Therefore, all these results indicate that polyindole nanofiber is more suitable to be used as an electrode active material in rechargeable battery compared with polyindole powder.

3.8. Mechanism

Based on above results, we propose a mechanism for this Li/polyindole nanofiber battery, as shown in Fig. 9. The electrochemical equations for charging and discharging processes can be formulated as following. In cell reaction a one-electron transform from polymer electrode has been assumed for simplicity.

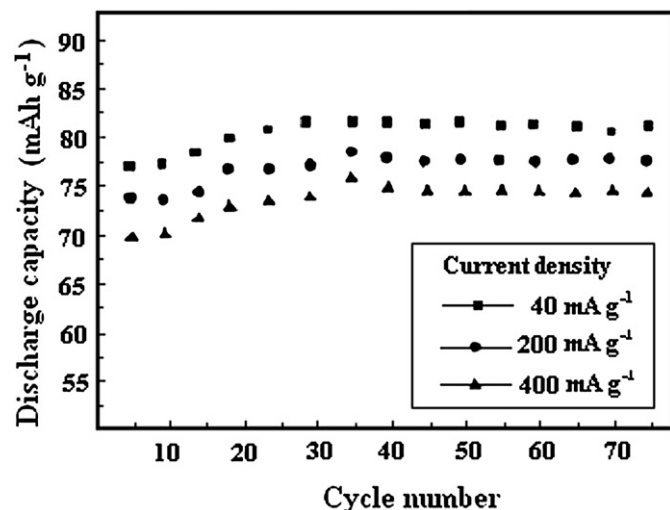


Fig. 8. The cyclic property of experimental Li/polyindole nanofiber cell at different current density.

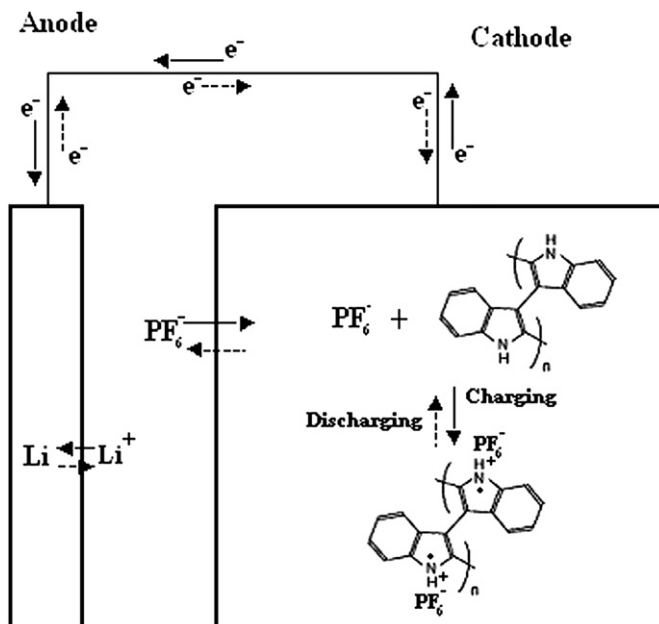
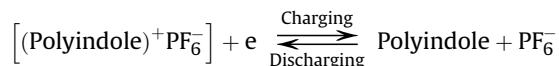
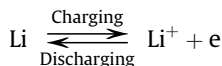


Fig. 9. The proposed charge/discharge mechanism of Li/polyindole nanofiber battery.

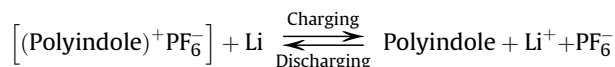
At cathode:



At anode:



Overall reaction:



During the charging process, the paired electrons at nitrogen site in polyindole are changed to unpaired electrons by the oxidation. The concentration of unpaired electrons increases and thereby the electrical conductivity increases. In discharge process, the reverse direction takes place.

4. Conclusion

A Li/polyindole nanofiber battery has been fabricated using polyindole nanofiber as cathode active materials, Li as anode active materials and LiPF_6 containing electrolyte solutions. Polyindole nanofiber was fabricated using electrospinning technique to make nanofibrous morphology. From SEM images, it is clear that the surface of cathode is porous and the diameter of the nanofiber is ranged from 347 nm to 180 nm. Cyclic voltammetry test results reveal that the doping and de-doping process of PF_6^- ions are reversible and polyindole nanofiber electrode has high electronic activity in the electrolytic solution containing LiPF_6 . The battery achieves 3.0 V electromotive force with discharge capacity of 83 mAh g^{-1} which is about 99% of theoretical value. There is slow capacity fading during cycling and the discharge capacity reaches 61 mAh g^{-1} at 500th cycle at low discharge current density. At higher discharge current density, the cell still can deliver stable discharge capacity. These results indicate that the Li/polyindole

nanofiber battery has very excellent cycle property as well as fast charge and discharge properties. Temperature has strong effect on the capacity of polyindole nanofiber cell. At elevated temperatures such as 60 °C the specific discharge capacity is near 120 mAh g⁻¹, which is about 45% higher than the capacity at 20 °C. Polyindole nanofiber has been proved to be a better candidate than polyindole powder as cathode material in lithium ion battery and would be promising in future applications.

Acknowledgments

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